Phosphorus speciation in a long-term manure-amended soil profile – evidence from wet chemical extraction, ^{31}P-NMR and P K-edge XANES spectroscopy

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Long-term application of manure may cause enrichment of phosphorus (P) in soils, posing a threat to surface water quality when this P is leached into drainage systems. The development of according risk assessment tools and mitigation strategies requires knowledge of the P species present in such soils. However, the speciation of P in soils remains challenging due to the complexity of the soil system and methodological limitations. We have applied ^{31}P-NMR and P K-edge XANES spectroscopy to characterise P in a soil that received manure for more than 40 years, and which is known for high P losses (Figure 1).

The topsoil P contents (40 mmol kg^{-1}) were greatly enhanced relative to the subsoil. According to linear combination fitting of XANES spectra, the P speciation in this soil was dominated by phosphate bound to iron (Fe) and aluminum (Al) mineral phases, with proportions of up to 76%. In the topsoil there was a substantial contribution also from amorphous calcium phosphate (30%). Deeper down, crystalline apatite increasingly gained importance with up to 79% at 80 cm depth, probably reflecting a lower degree of weathering in the subsoil. The topsoil organic P content was low (max. 14%) and dominated by P monoesters, according to NMR spectroscopy. In conclusion, the results show that P from the manure was bound mostly to Fe and Al in the soil; however, the low content of oxalate-extractable Fe + Al (< 80 mmol kg^{-1} in the topsoil) implies that the P sorption capacity was small and that therefore, P was susceptible to leaching.

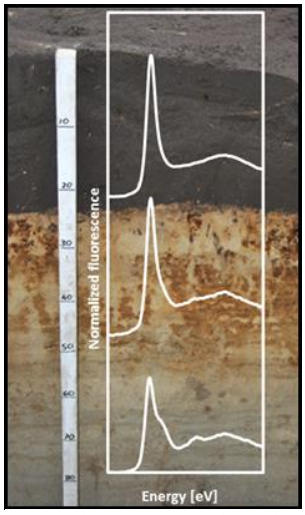

Figure 1: P K-edge XANES spectra of soil samples at 0-30, 40-50, and 70-80 cm depth